Chiral Polyfluorene Derivatives: Synthesis, Chiroptical Properties, and Investigation of the Structure−Property Relationships

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ABSTRACT: Four polyfluorene derivatives with chiral center in the backbone or at the side chain, **P*L*PheF** (**P1**), **P*L*PhGlyF** (**P2**), **P*D*PheF** (**P3**), and **PSPF** (**P4**), have been designed and synthesized through the Pd-catalyzed Suzuki polymerization. The structures of these polymers are characterized by ^{1}H and ^{13}C NMR, UV−vis, photoluminescence (PL), and CD spectroscopic methods as well as elemental analysis. These four polymers exhibit the linearly polarized photoluminescence in dilute solutions. The investigation of the absorption and emission behaviors indicates that the aggregates and/or the excited states excimers might be formed in THF solution at higher concentrations. We also observe the emission dichroic ratio R_{PL} of these polymers in films is increased in comparison with that in solutions. After film annealing, polymers **P1**, **P2**, and **P3** also show obvious linearly polarized photoluminescence at 500−650 nm. Moreover, the films of polymer **P4** exhibit good thermal spectral stability after annealing in comparison with other three polymers **P1**, **P2**, and **P3**. We also report the circular dichroism (CD) spectroscopic properties of these four polymers in THF solutions.

Introduction

π-Conjugated polymers have attracted more considerable interest due to their electronic and photonic applications, such as organic field effect transistors (OFETs), organic light-emitting diodes (OLEDs), photovoltaics, and organic lasers as well as other organic devices.[1] Inside these organic devices, π-conjugated polymers are fabricated as very thin films (about 50−100 nm) by spin-casting or inkjet printing from their dilute solutions. It has been demonstrated that properties of materials depend on film morphology at an extent scale from macroscopic down to microscopic (a few angstroms), as determined by polymer structure and film processing conditions.[2] One important feature of conjugated materials is the potential for controlling macroscopic photophysical properties by manipulating the order or orientation of the molecules. Therefore, considerable interests have been devoted to the design, synthesis, and characterization of chiral conjugated oligomers and polymers directed at the formation of helices, twisted ribbons, and cholesteric mesomorphism both in solutions and in neat films in the past decades.[3] Some positive results have been achieved from developing novel conjugated polymers carrying chiral pendants including poly(thiophene) (PT),[4] poly(*p*-phenylenevinylene) (PPV),[5] poly(fluorene-2,7-diyl) (PF),[6] poly(*p*-phenylene) (PPP),[7] poly(acetylene) (PA),[8] and poly(*p*-phenyleneethynylene) (PPE)[9] derivatives and understanding their corresponding supramolecular structures through the formation of chiral structures supported by both circular dichroism and circularly polarized fluorescence.[10]

To facilitate film processing for practical application and to systematically investigate structure−property relationships, it is of particular interest to develop new chiral conjugated polymers. Of all the conjugated systems that have been explored, oligo- and polyfluorene derivatives are promising materials for OLEDs, especially because of their blue and strong electroluminescence (EL) and the good solubility in organic solvents.[11] Polyfluorene (PFs) derivatives easily form the homogeneous layers with solution-based coating techniques. Introduction of two chiral side chains at the 9-position of the fluorene units of polyfluorenes are found to result in large circular polarization in the absorption and emission of the desired derivatives. The films of chiral oligo- and polyfluorenes exhibit extraordinary chiroptical properties suitable for fabrication of the devices with circularly polarized electroluminescence (CPEL), which might be served as backlights for liquid crystal display.[6,12] However, up to now, there were few reports on circularly polarized emission and electroluminescence from polyfluorene derivatives with the chiral backbone of the polymer, and the effect of the chiral centers of polyfluorene derivatives on their photophysical properties.[13]

Herein, we present the synthesis and the photophysical properties of chiral polyfluorene derivatives, in which the chiral centers are in the side chain and in the backbone of polymers, respectively. Pu et al. developed novel rigid and sterically regular polymeric catalysts employing optically active 1,1′-binaphthyl at the main chain, which exhibited good enantioselectivies in organic asymmetric synthesis and good electroluminescence properties for OLEDs.[14] In this contribution, we not only develop three polyfluorene derivatives containing chiral bisoxazoline at the side chain (**P1**, **P2**, and **P3**), but also prepare a polymer containing optically pure 9,9′-spirobifluorene units at the backbone (**P4**). The linearly polarized photophysical properties of these four polymers both in various solutions and in thin films are investigated. The circular dichroism (CD) properties and linearly polarized photoluminescence spectra of polyfluorenes with different chiral alkyl side chains and backbones are discussed with respect to intra- and interchain contributions to the chiroptical response. After these films were

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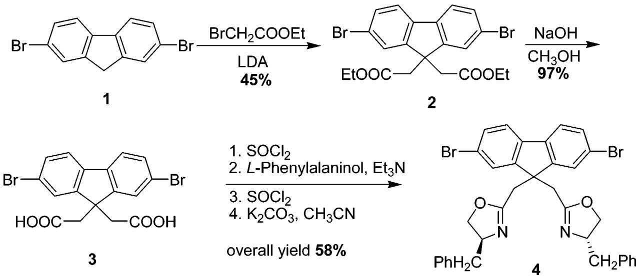
Scheme 1



annealed, the intensity of the long wavelength emission increased for both the normal photoluminescent and linearly polarized photoluminescent behaviors of polymers **P1**, **P2**, and **P3** in solid states. However, polymer **P4** exhibits no change both in the normal emission and in the linearly polarized photoluminescent behaviors in solid states.

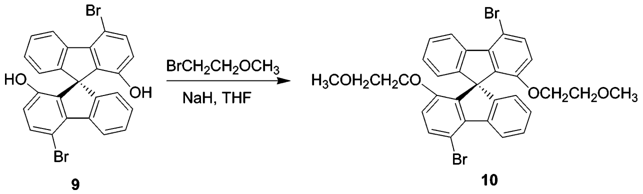
Results and Discussions

Synthesis. Scheme 1 illustrates the synthetic approach to monomer **4**. The reaction of **1** with ethyl bromoacetate in the presence of lithium diisopropylamine (LDA) afforded compound **2** in moderate yield (45%), which followed by the hydrolyzation to give diacid **3** in high yield (97%). The typical processes of preparing bisoxazoline from **3** in four steps was followed and produced a new bisoxazoline derivative **4** in 58% overall yield (also in Scheme 1).[15]

The synthetic approach to monomers **8a** and **8b** is shown in Scheme 2. Reduction of **2** with lithium aluminum hydride formed diol **5** in high yield (94%). Treatment of **5** with I$_2$, imidazole and PPh$_3$ led to the formation of **6** in moderate yield (54%). To improve the yield of the preparation of bisoxazoline derivatives, we also employed manolonitrile as a starting material to prepare bisoxozalines **7a** and **7b** by two steps according to the published procedures.[16] Condensation of **6** and **7a** or **7b** in the presence of lithium diethylamine produced the spirobisoxazoline monomers **8a** and **8b**, respectively.

The enantiomerically pure spirobifluorene diol **9**, whose preparation procedure was developed in our group,[17] reacted with 1-bromide-2-methoxyethane to produce another Suzuki coupling precursor **10** as shown in Scheme 3. Finally, the Suzuki coupling polymerization of **4**, **8a**, **8b**, and **10** with 2-(9,9-dihexylfluorenyl)^{1,3,2}dioxaborolane catalyzed by Pd(PPh$_3$)$_4$ produced the desired polymers **P1**, **P2**, **P3**, and **P4**, respectively (as illustrated in Scheme 4). Among these polymers, the chiral units at the side chain of **P1** and **P3** were enantiomers, and the system of **P4** was referred to as an axial chirality.

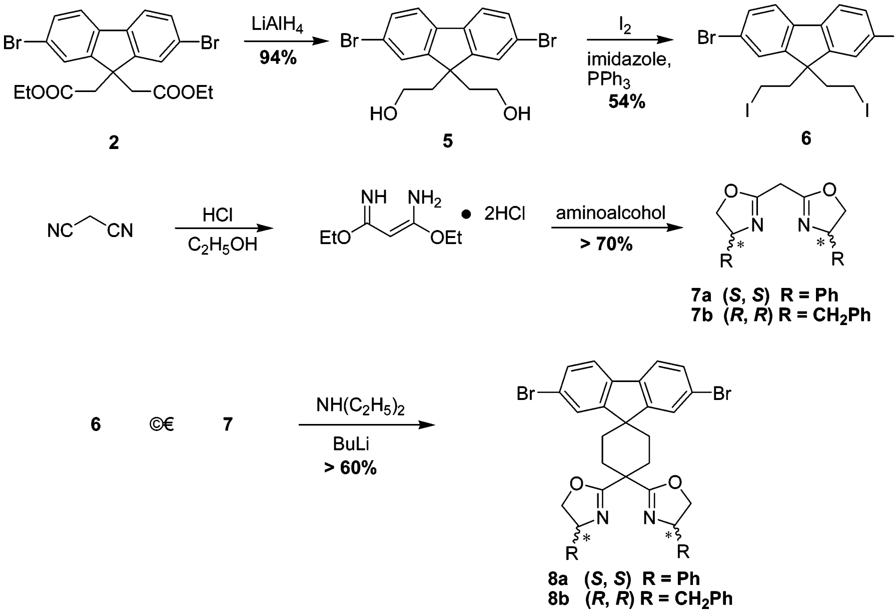
Scheme 3



The crude polymers were washed with methanol, water, and methanol again, successively, and were placed in a Soxhlet apparatus and extracted with refluxed acetone for 48 h, and then was dried at 60 °C in vacuum oven. These polymers were readily soluble in common organic solvents, such as THF, CHCl$_3$, toluene, xylene, etc, which provided us the convenience to obtain the ^{1}H and ^{13}C NMR spectra of these polymers and their photophysical properties in solutions. The molecular structure of these polymers was verified by ^{1}H and ^{13}C NMR spectroscopy and elemental analysis. The molecular weights of polymers **P1**, **P2**, **P3**, and **P4** were determined by gel permeation chromatography (GPC) with THF as the eluent, calibrated against polystyrene standards. As shown in Table 1, the GPC analysis indicated that the number-average molecular weight (M_n) and polydispersity index (PD) of the polymers were in the ranges from 9459 to 18 699 and from 1.5 to 2.4, respectively.

Thermal Stability. The thermal stability of polymers **P1**−**P4** was investigated by thermogravimetric analysis (TGA) under nitrogen atmosphere and in air. All polymers exhibited outstanding thermal stability with onset degradation temperatures (T_d) above 300 °C under nitrogen atmosphere. In air, the onset degradation temperature of these four polymers was above 260 °C. The average T_d of these polymers up to 400 °C was similar to that of poly(9,9-dihexylfluorene-2,7-diyl) (**PDHF**), suggesting that both the incorporation of chiral moiety and the unique molecular structure did not affect the thermal stability. The thermally induced phase transition behaviors of these chiral

Scheme 2



Scheme 4

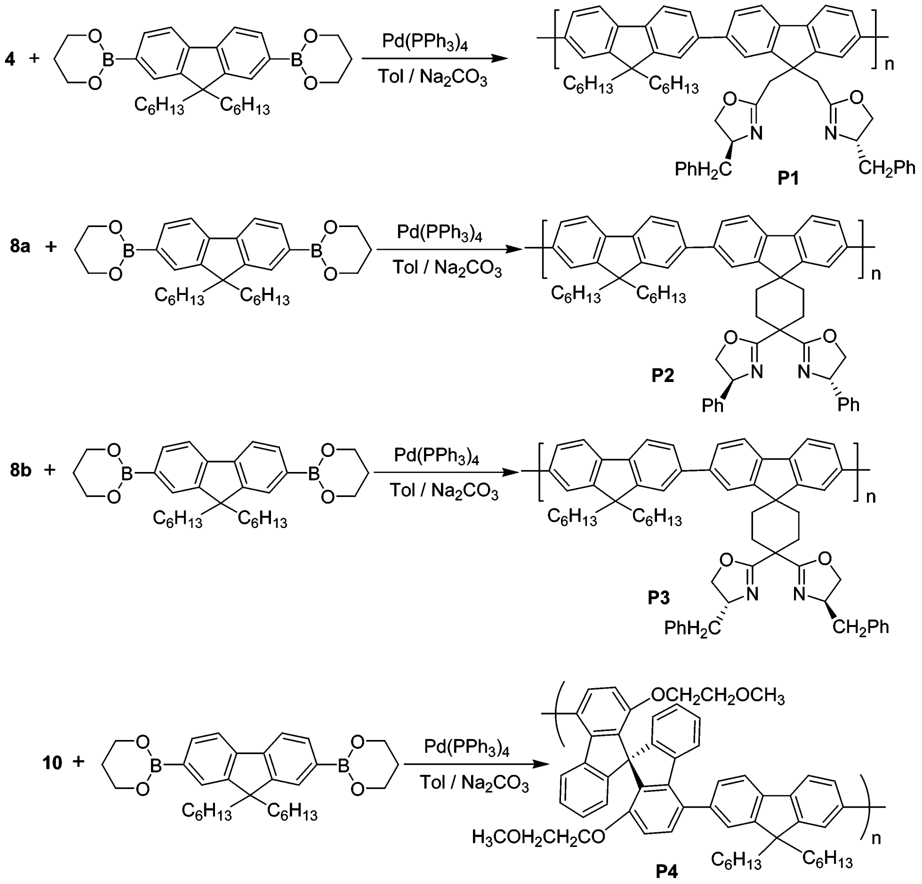


Table 1. Molecular Weight and Phase Transition Temperatures of Polymers P1, P2, P3, and P4.

polymers	M_n	M_w	PD	T_g (°C)
P1	11 709	17 310	1.5	114
P2	9459	14 703	1.6	161
P3	18 699	45 797	2.4	142
P4	10 383	16 347	1.6	155

polymers were determined by differential scanning calorimetry (DSC) under nitrogen atmosphere at a heating rate of 10 °C min^{-1}. The results are illustrated in Figure 1 and summarized in Table 1. We observed that the introduction of the chiral moieties effectively improved the T_g temperature of the polymers **P1**−**P4** (114−161 °C) in comparison with that of **PDHF** (about 104 °C).[18] We also observed that such an introduction of chiral units into the polymers did not obviously affect the amorphous states of the polymers, which was due to the rigid backbone and cyclic side chain. The T_g temperatures of polymers **P2** and **P3** were higher than that of **P1**, which might be due to the rigid cyclohexyl structure in polymers **P2** and **P3.**

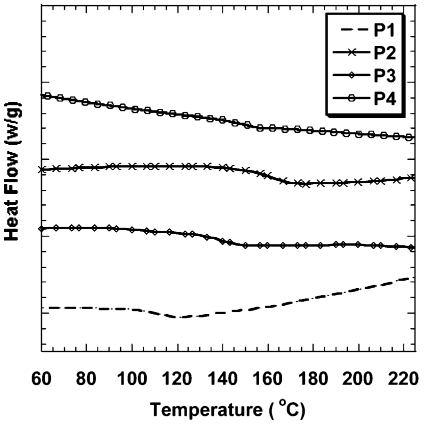


Figure 1. DSC behaviors of polymers **P1**, **P2**, **P3**, and **P4**.

Table 2. UV−Visible and Photoluminescence Spectra of P1, P2, P3, and P4 in Dilute THF Solutions and in Film States at Room Temperature.

polymers	abs λ_{max} (nm) solution	emission (nm)	R_{PL}	abs λ_{max} (nm) film	emission (nm)	R_{PL}	R_{PL}[a]
P1	381	418	2.0	385	430	5.3	5.1
P2	383	418	2.0	384	430	4.1	4.1
P3	391	418	1.9	393	430	4.0	3.8
P4	325	398	1.8	326	408	3.1	3.4

[a] After annealing.

Photophysical Properties. The normalized absorption spectra of polymers **P1**, **P2**, **P3**, and **P4** in dilute THF solutions (about 10^{-6} M) are shown in Figure 2. The photophysical properties of these polymers both in dilute solutions and in thin films are summarized in Table 2. Normally, π-conjugated polymers show a very strong $\pi-\pi^*$ electron absorption band in the UV−vis region, which progressively red-shifted with increase of effective conjugation length. From absorption spectra illustrated in Figure 2, we observed that polymer **P1**, **P2**, and **P3** exhibited the similar absorption λ_{max} (381 nm for **P1**, 383 nm for **P2**, and 393 nm for **P3**, respectively), in which the absorption peak of **P3** exhibited a small red-shift (about 10 nm) in comparison with those of **P1** and **P2** although the absorption spectra of these four polymers showed the same onset. Such absorption behaviors in solutions were similar to those of poly(9,9-dialkylfluorene-2,7-diyl).[19] However, the absorption behaviors of **P4** peaked at 325 nm, which blue-shifted about 60 nm in comparison with those of **P1**, **P2**, and **P3**. This was due to the sp^3 carbon

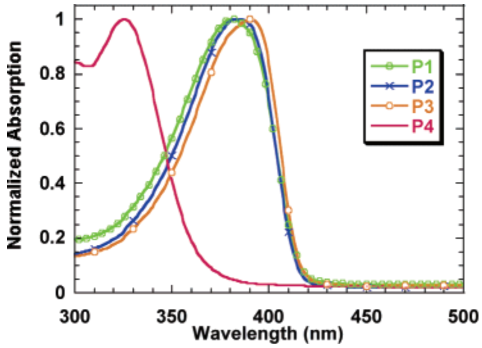


Figure 2. Normalized absorption spectra of **P1**, **P2**, **P3**, and **P4** in dilute THF solutions.

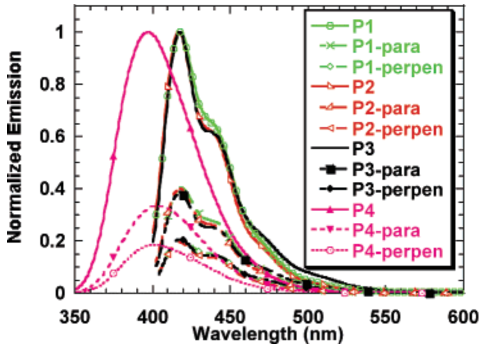


Figure 3. Normalized emission spectra of **P1**, **P2**, **P3**, and **P4** in dilute THF solutions. Emission spectra were obtained upon excitation at the absorption maximum.

at C9-position of spirobifluorene unit in the backbone, which interrupted the increase of effective conjugated length.[20]

The photoluminescent (PL) emission spectra of **P1**, **P2**, **P3**, and **P4** in dilute THF solutions, excited at absorption maximum wavelength, are illustrated in Figure 3. Polymers **P1**, **P2**, and **P3** showed almost identical behaviors, which peaked at 418 nm with a shoulder at 426 nm. Such PL spectra were also similar to those of poly(9,9-dialkylfluorene-2,7-diyl).[19] These three polymers also exhibited very small Stokes shift (about 25−35 nm) between 0 and 0 transition of absorption and emission indicating a small structural reorganization in the excited state. However, for polymer **P4**, the emission features peaked at 398 nm, which blue-shifted about 20 nm in comparison with those of **P1**, **P2**, and **P3**, which was also due to the sp^3-carbon at the C9-position of spirobifluorene unit in the backbone although the stokes shift of **P4** between 0 and 0 transition of absorption and emission was about 63 nm, which indicated the structural reorganization might be formed in the excited state. We also investigated the linearly polarized photoluminescence of these four polymers in dilute THF solutions. Figure 3 also illustrates the linearly polarized photoluminescent behaviors in solutions. It was observed that the photoluminescence of these four polymers was linearly polarized. The emission peak dichotic ratio, defined as $R_{PL} = E_{\|}/E_{\perp}$ where $E_{\|}$ and $E_{\perp}$ denote the emission intensity at the parallel and perpendicular director, respectively, are summarized in Table 2. As shown in Figure 3, we observed that the parallel emission intensity$E_{\|}$ were higher than the perpendicular intensity $E_{\perp}$ for every polymer. These results might be related to conformational changes upon photoexcitation or to emission from polymer chains.

We also investigated the absorption spectra and emission behaviors of polymers **P1**, **P2**, **P3**, and **P4** in THF solutions at low and high concentrations at room temperature. We observed a little change from their absorption in THF solution when the concentration was enhanced from 10^{-7} to 10^{-3} M, while the obvious red-shift showed in their PL spectra when the concentration was 10^{-3} M. For **P1**, the PL spectra in THF solution at the concentrations between 10^{-7} and 10^{-5} M were identical; however, when the concentration was 10^{-4} M, the emission λ_{max} red-shifted from 418 to 433 nm, and further red-shifted to 445 nm when the concentration increased to 10^{-3} M, and we also observed that the emission at long wavelength (about 520 nm) was obviously enhanced. For polymers **P2** and **P3**, we also observed that the emission spectra were almost identical at the concentrations between 10^{-7} and 10^{-5} M. Moreover, the emission λ_{max} red-shifted about 24 nm with the increase of the concentrations from 10^{-5} to 10^{-3} M. However, the emission at long wavelength did not obviously increased. For **P4**, although the emission behaviors were almost indistinguishable at the concentration between 10^{-7} and 10^{-5} M, the emission λ_{max} red-shifted about 13 nm when the concentration increased to 10^{-3} M, which were similar as those in the film. These results demonstrated that these polymers were formed the aggregates and/or the excited-state excimers in THF solutions at higher concentrations above 10^{-3} M, which was similar as poly[2,7-{9,9-bis[(*S*)-3,7-dimethyloctyl]}fluorene] (PFMO).[13]

Uniform polymer films were prepared on a quartz glass substrate by spin-coating from solution in toluene (2% w/v) at a spin rate of 2000 rpm. The thickness of all films was about 80−100 nm. The normalized absorption and emission spectra of polymers **P1**, **P2**, **P3**, and **P4** in films are shown in Figures 5 and 6, respectively. The absorption spectra of four polymers in solid states were quite similar to those in dilute solutions with slight red shift. This indicated that polymers **P1**, **P2**, and **P3** did not form the obvious aggregation in the ground states after the introduction of the chiral units in the side chain. For polymer **P4**, the tetrahedron conformation of sp^3 carbon at the spiro center of spirobifluorene units effectively reduced the possibility of the aggregation in the ground state.

For their emission behaviors in solid states, as shown in Figure 6, **P1**, **P2**, and **P3** exhibited the typical spectral features of polyfluorene homopolymers with the well-defined vibronic structure. The bright blue emission with two vibronic peaks at 430 and 445 nm was observed, which were slightly red-shifted compared with those in solutions. In comparison with the emission behaviors of **P2** and **P3**, the long wavelength emission from the PL behaviors of **P1** in the fresh prepared films was observed, which might be owing to the shorter side chain in polymer **P1**. However, for the emission spectrum of **P4**, the nonstructureless feature peaked at 408 nm. The linearly polarization photoluminescent features in thin films are illustrated in Figure 6. The photoluminescence of these four polymers exhibited the obvious linear polarization. The degree of linearly polarization using emission peak dichotic ratio R_{PL} value was summarized in Table 2, which was enhanced in comparison with that of in solutions. For example, the emission peak dichotic ratio R_{PL} value of **P1** in film increased from 2.0 to 5.3 in comparison with that in solution. For **P4**, the emission peak dichotic ratio R_{PL} value in film was about 3.1.

The emission spectrum stability upon thermal annealing is critical character for OLEDs, since the temperature inside the devices could increase depending on the operation conditions. It is well-known that when PF films were heated with exposure to air, an additional broad, featureless band emerged and increased, resulting in a decreased efficiency as well as changing the pure blue emission to an undesirable blue-green color.[19] After the films of our four polymers were annealed, as shown in Figure 7, the long wavelength emission of polymers **P1**, **P2**, and **P3** obviously was enhanced, which was identical with

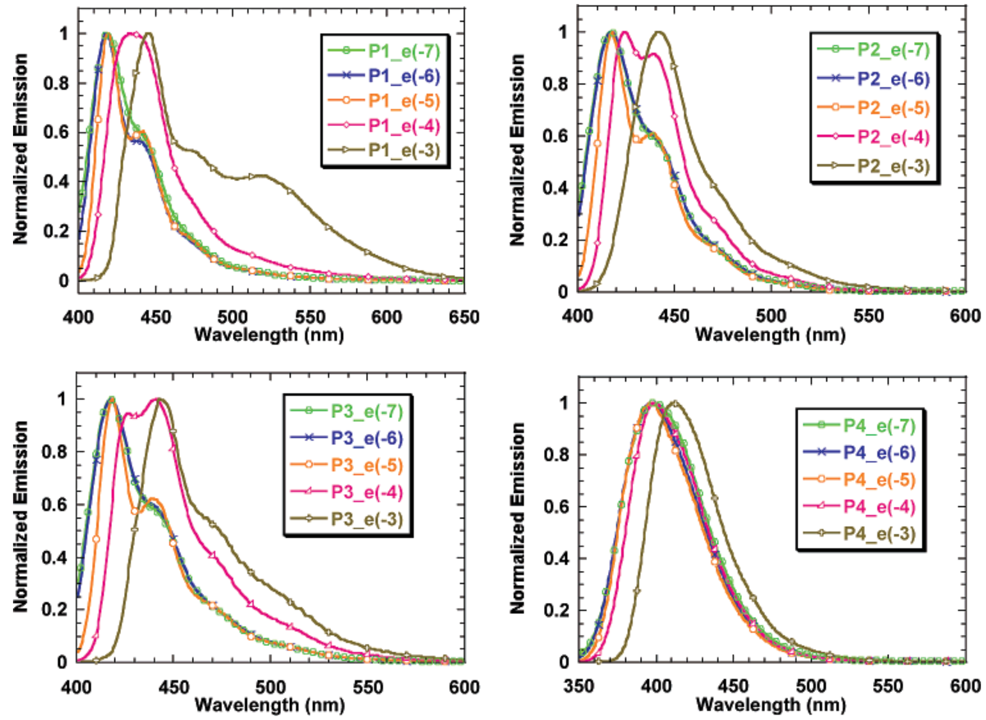


Figure 4. Normalized emission spectra of **P1**, **P2**, **P3**, and **P4** in THF at various concentrations. Emission spectra were obtained upon excitation at the absorption maximum.

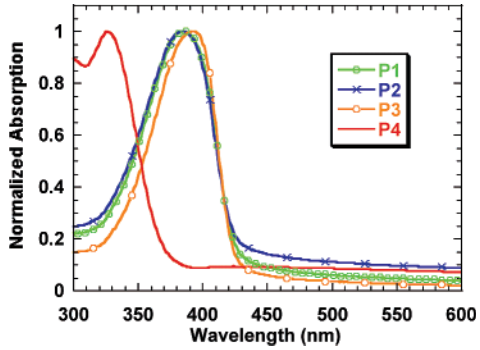


Figure 5. Normalized absorption spectra of **P1**, **P2**, **P3**, and **P4** in solid states.

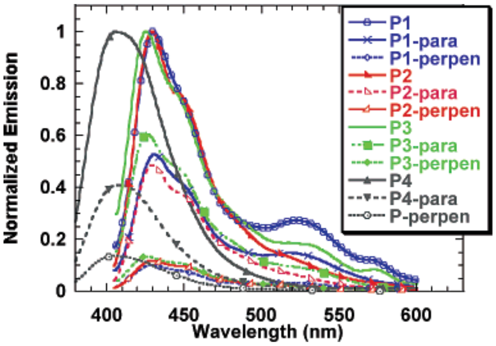


Figure 6. Normalized emission spectra of **P1**, **P2**, **P3**, and **P4** in solid states. Emission spectra were obtained upon excitation at the absorption maximum.

normal dialkyl-substituted polyfluorene derivatives, although the long wavelength emission exhibited the linearly polarization photoluminescent features. However, for **P4**, we did not observe any long wavelength emission from its PL spectra after annealing the film above its T_g temperature for 24 h. The R_{PL} value exhibited a little change from 3.1 to 3.4. Such results demonstrated that polymer **P4** might be a promising candidate for chiral blue emitting material.

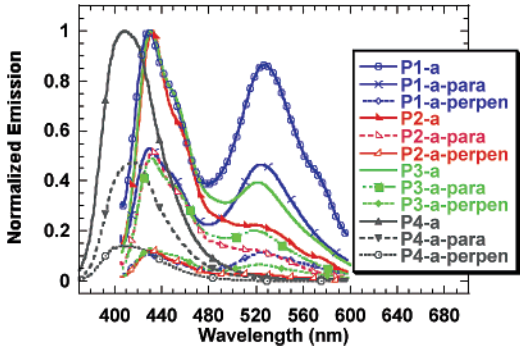


Figure 7. Normalized emission spectra of **P1**, **P2**, **P3**, and **P4** in solid states after annealing. Emission spectra were obtained upon excitation at the absorption maximum.

The circular dichroism (CD) behaviors of these four polymers in dilute THF solution were also investigated. CD has proved to be a very powerful tool for the determination of helical conformations of polymers. Figure 8 outlines the CD behaviors of all four polymers in solutions. The CD spectra of all polymers **P1**−**P4** in THF solutions revealed a typical Cotton effect at the $\pi-\pi^*$ transition which exhibited vibrational fine structure. The CD effect from interchain exciton coupling demonstrates that the induction of the chiral units effectively enhanced the helical conformation of individual polymer chains. We believe that the optical activity resulted from a chiral orientation of the polymer chain and CD behaviors originated from a helical intrachromophore and interchromophore conformation further enhanced by the chiral units although these polymers owned the essentially planar chains. It was observed that **P4** having an axial chirality at the polymer backbone showed an extremely higher CD response than other three polymers **P1**, **P2**, and **P3**. Furthermore, the CD effect of polymer **P1** was opposite with that of **P3** because the chiral units at the side chains of **P1** and **P3** were enantiomers.

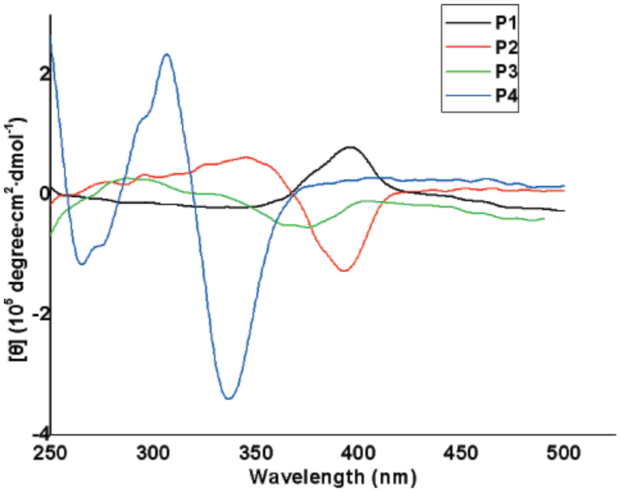


Figure 8. Circular dichroism spectra of polymers **P1**, **P2**, **P3**, and **P4** in dilute THF solutions.

Conclusion

In conclusion, we synthesize four new chiral polyfluorene derivatives **P1**, **P2**, **P3**, and **P4** through the Suzuki polymerization. This is the first time to synthesize the chiral helical conjugated polymers with optically active 9,9-spirobifluorene skeleton at the polymer backbone. These polymers exhibit the obvious linearly polarized photoluminescent properties both in solutions and in thin films. The investigation of the PL emission behaviors of these four polymers in THF solution at various concentrations indicates that the aggregates and/or the excited-state excimers might be formed in THF solution at the higher concentration. The investigation of CD effect demonstrates that **P4** having an axial chirality at the backbone exhibits the higher Cotton features than other three polymers **P1**, **P2**, and **P3**. We also investigate the linearly polarized photoluminescent properties of the thin films of four polymers after annealing. Although it is exhibited in the PL spectra of polymers **P1**, **P2**, and **P3**, this long wavelength emission at about 500−600 nm is also the circular polarization with the same R_{PL} value as the linearly polarized emission at 418 nm. However, such long wavelength emission has not been observed from the emission behaviors of **P4** in thin films after annealing. These results demonstrate that **P4** could be a promising candidate as a stable circular polarized blue-emitting conjugated polymer for circular polarized OLEDs.

Experimental Section

General Methods. Chemicals were purchased from Acros and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Mercury plus 300 MHz using $CDCl_3$ or DMSO-d_6 as solvent in all cases. UV−vis spectra were recorded on Perkin-Elmer Lambda 35 UV−vis spectrometer. PL spectra were carried out on a Perkin-Elmer LS55 Luminescence spectrometer. DSC was performed on a Mettler DSC 822^e module in conjugated with a Mettler Thermal Analyst STAR^e system under a heating rate of 10 °C/min and the nitrogen flow rate of 60 cm^3/min.

Compound 2. To a solution of LDA (73 mmol) in anhydrous THF was added 2,7-dibromofluorene (10.8 g, 33.3 mmol) under nitrogen atmosphere at −78 °C. After 15 min, ethyl bromoacetate (13.2 g, 79 mmol) in anhydrous THF was added dropwise. The mixture was warmed to room temperature and stirred overnight. The mixture was quenched with aqueous NH_4Cl, and the aqueous layer was extracted with ethyl acetate. The combined extract was washed with H_2O, brine and dried over anhydrous $MgSO_4$. After the solvents were removed under vacuum, the residue was purified by column chromatography using ethyl acetate/petroleum ether as the eluent to afford 7.4 g (45%) of paint yellow solids. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.67−7.68 (d, J = 1.8 Hz, 2H, Ar−H), 7.50−7.53 (m, 4H, Ar−H), 3.91−4.00 (q, 4H, J = 7.2 Hz, $O-CH_2$), 3.02 (s, 4H, CH_2-CO), 1.02−1.08 (t, 6H, J = 6.9 Hz, CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 169.9, 150.3, 138.1, 131.2, 127.3, 121.5, 121.3, 60.4, 49.9, 41.7, 13.9. EI MS (*m/z*): 494 (M^+). Anal. Calcd for $C_{21}H_{20}Br_2O_4$: C: 50.83; H: 4.06. Found: C: 50.91; H: 4.08.

Compound 3. To a solution of **2** (2.5 g, 5.0 mmol) in CH_3OH (25 mL) was added 12 mL of aqueous NaOH solution (2 N). After being refluxed for 8 h, the mixture was cooled to 0 °C and neutralized with aqueous HCl. The mixture was extracted with ethyl ether. The extracts were washed with aqueous $NaHCO_3$ solution and brine, and then dried over anhydrous $MgSO_4$. After evaporation of the solvents under vacuum, the residue was washed with 10 mL of $CHCl_3$ to afford 2.1 g (97%) of light yellow solids. ^{1}H NMR (DMSO-d_6, 300 MHz, ppm): δ 12.00 (s, 2H, COOH), 7.82−7.85 (d, 2H, J = 1.8 Hz, Ar−H), 7.74−7.79 (d, 2H, J = 8.1 Hz, Ar−H), 7.48−7.54 (dd, 2H, J = 8.1 Hz, 1.8 Hz, Ar−H), 3.06 (s, 4H, CH_2). ^{13}C NMR (DMSO-d_6, 75 MHz, ppm): δ 171.1, 151.4, 138.6, 130.4, 126.8, 122.1, 120.5, 49.9, 41.9. EI MS (*m/z*): 438 (M^+). Anal. Calcd for $C_{17}H_{12}Br_2O_4$: C: 46.40, H: 2.75. Found: C: 46.09, H: 2.81.

Compound 4. Compound 3 (1.9 g, 4.3 mmol) was refluxed with $SOCl_2$ (10 mL) for 2 h. After removal of the excess $SOCl_2$, the residue was dissolved in 10 mL of CH_2Cl_2 and added dropwise to a mixture of *L*-phenylalaninol (1.6 g, 9.7 mmol) and Et_3N (3 mL, 22 mmol) in 10 mL of CH_2Cl_2 at 0 °C. The mixture was stirred at room temperature for 8 h. The reaction mixture was washed with brine. The organic layer was dried over anhydrous Na_2SO_4. After removal of the solvents, purification by column chromatography (ethyl acetate/petroleum ether = 1/1) afforded a crude product. The crude product was dissolved in 10 mL of $SOCl_2$ and then refluxed for 2 h. After removal of the excess $SOCl_2$ under vacuum, the residue was dissolved in 20 mL of CH_3CN, and then K_2CO_3 (1 g, 7.2 mmol) and several drops of water were added to the mixture. The mixture was refluxed overnight. The precipitate was filtered and washed with CH_2Cl_2. After removal of the solvent under vacuum, the residue was purified by column chromatography using ethyl acetate/petroleum ether as eluent to afford 1.7 g of product (yield: 58%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.70 (s, 2H, Ar−H), 7.47 (m, 4H, Ar−H), 7.00−7.40 (m, 10H, Ph), 4.10−4.25 (m, 2H, CH−N), 3.80−4.00 (t, 2H, J = 8.4 Hz, CH_2-O), 3.50−3.70 (t, 2H, J = 8.4 Hz, CH_2-O), 3.03−3.15 (d, 2H, J = 14.7 Hz, CH_2−Box), 2.94−3.00 (d, 2H, J = 14.7 Hz, CH_2−Box), 2.70−2.90 (dd, 2H, J = 13.2 Hz, 2.4 Hz, CH_2), 2.20−2.40 (dd, 2H, J = 2.4 Hz, 13.2 Hz, CH_2). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 163.6, 149.9, 137.9, 137.7, 130.8, 128.8, 128.2, 127.6, 126.1, 121.0, 120.8, 71.3, 67.0, 50.9, 41.6, 36.1. EI MS (*m/z*): 668 (M^+). Anal. Calcd for $C_{35}H_{30}Br_2N_2O_2$: C: 62.70, H: 4.51, N: 4.18. Found: C: 62.54, H: 4.65, N: 4.05.

P1. To a mixture of 1.5 mol % of $Pd(PPh_3)_4$ in 10 mL of degassed toluene and 6 mL of 2 M aqueous sodium carbonate solution was added 9,9-dihexylfluorene-2,7-bis(trimethylene boronate) (0.50 g, 1 mmol) and **4** (0.67 g, 1 mmol). The mixture was vigorously stirred under a nitrogen atmosphere at 80−90 °C for 72 h. The mixture was poured into 100 mL of methanol with stirring to precipitate solids. The solid was collected by filtration and washed with methanol and water. The polymer was further purified by washing with refluxing acetone in Soxhlet for 2 days, and was dried under vacuum at room temperature to afford 0.49 g (58%) of a light yellow solid. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.40−8.00 (m, 10H, Ar−H), 6.80−740 (m, 12H, Ar−H), 4.10−4.36 (m, 2H, CH−N), 3.84−4.05 (m, 2H, CH_2-O), 3.50−3.72 (m, 2H, CH_2-O), 3.12−3.44 (m, 4H, CH_2Ph), 2.66−2.96 (m, 2H, CH_2), 1.90−2.35 (m, 6H, CH_2), 0.40−1.25 (m, 22H, C_5H_{11}). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 164.8, 151.8, 149.4, 140.4, 139.3, 137.9, 129.0, 128.4, 127.2, 126.3, 123.2, 121.4, 120.0, 71.7, 67.2, 55.4, 51.2, 41.9, 40.6, 36.9, 31.5, 29.8, 23.9, 22.6, 14.0. Anal. Calcd for $C_{60}H_{62}N_2O_2$: C: 85.47, H: 7.41, N: 3.32. Found: C: 84.23, H: 7.36, N: 3.00.

Compound 5. A solution of **2** (9.9 g, 20 mmol) in 50 mL of anhydrous ethyl ether was added dropwise to a solution of $LiAlH_4$ (0.76 g, 40 mmol) in 50 mL of anhydrous ethyl ether. The mixture was refluxed for half an hour and then saturated Na_2SO_4 solution was added dropwise. The precipitate was filtered and washed with ether. After removal of the solvent under vacuum, the residue was purified by column chromatography using ethyl acetate to afford 7.7 g (94%) of the products as a white powder. ^1H NMR (DMSO-d_6, 300 MHz, ppm): δ 7.70–7.90 (m, 4H, Ar–H), 7.44–7.60 (m, 2H, Ar–H), 4.10–4.30 (t, 2H, $J = 5.1$ Hz, OH), 2.56–2.76 (m, 4H, CH_2), 2.15–2.36 (t, 4H, $J = 7.5$ Hz, CH_2). ^{13}C NMR (DMSO-d_6, 75 MHz, ppm): δ 151.8, 138.1, 130.2, 126.4, 122.1, 121.0, 56.5, 52.0. EI MS (*m/z*): 410 (M^+). Anal. Calcd for $C_{17}H_{16}Br_2O_2$: C: 49.54, H: 3.91. Found: C: 49.34, H: 4.05.

Compound **6.** To the solution of **5** (4.96 g, 10 mmol) were added imidazole (1.6 g, 24 mmol) and PPh_3 (5.5 g, 21 mmol) in 100 mL of CH_2Cl_2 in I_2 (5.3 g, 21 mmol) slowly. The mixture was stirred overnight and 30 mL of petroleum ether was added in. The precipitate was filtered. The organic layer was evaporated to remove the solvent. The crude product was purified by column chromatography to afford 3.4 g (54%) of the product as a white solids. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.50–7.55 (m, 6H, Ar–H), 2.57–2.70 (m, 4H, CH_2), 2.25–2.36 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 147.9, 139.19, 131.6, 126.1, 122.4, 121.7, 59.2, 44.2, −2.7. EI MS (*m/z*): 630 (M^+). Anal. Calcd for $C_{17}H_{14}Br_2I_2$: C: 32.31, H: 2.23. Found: C: 32.21, H: 2.34.

General Procedure for 8a and 8b. To a solution of diethylamine (1.09 g, 15 mmol) in 30 mL of THF at 0 °C was added BuLi (7 mL, 15 mmol) in hexane. The mitxture was stirred for half an hour and then cooled to −78 °C. A solution of **7a** (1.58 g, 5 mmol) in 15 mL of THF was added dropwise. The mixture was stirred at −20 °C for 30 min, and then cooled to −70 °C again; **6** (3.1 g, 5 mmol) was added in. The mixture was stirred at room temperature for an additional 16 h, and then it was quenched with saturated aqueous NH_4Cl solution. The mixture was extracted with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$. After removal of the solvents, the residue was purified by column chromatography (Al_2O_3, hexane/EtOAc) to give 2.3 g of the product as a white solid (68%). ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.73 (s, 2H, Ar–H), 7.31–7.58 (m, 14H, Ar–H), 5.38–5.44 (dd, 2H, $J = 7.5$ Hz, 9.9 Hz, CH–N), 4.77–4.84 (dd, 2H, $J = 8.4$ Hz, 9.9 Hz, OCH_2), 4.28–4.34 (t, 2H, $J = 8.2$ Hz, OCH_2), 2.74–2.80 (m, 2H, CH_2), 2.57–2.66 (m, 2H, CH_2), 2.00–2.05 (m, 2H, CH_2), 1.85–1.95 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 168.5, 153.7, 142.3, 137.6, 130.6, 128.9, 127.8, 127.7, 126.6, 121.2, 77.4, 77.0, 76.6, 75.3, 69.7, 49.8, 42.3, 31.4, 28.5. EI MS (*m/z*): 680 (M^+). Anal. Calcd for $C_{36}H_{30}Br_2N_2O_2$: C: 63.36, H: 4.43, N: 4.10; Found: C: 63.04, H: 4.52, N: 4.01.

Compound 8b. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.71 (d, 2H, $J = 1.5$ Hz, Ar–H), 7.40–7.59 (m, 6H, Ar–H), 7.21–7.34 (m, 10H, Ph), 4.52–4.62 (m, 2H, CH–N), 4.25–4.32 (t, 2H, $J = 8.7$ Hz, OCH_2), 4.09–4.15 (dd, 2H, $J = 6.9$ Hz, 8.4 Hz, OCH_2), 3.20–3.27 (dd, 2H, $J = 4.8$ Hz, 13.5 Hz, CH_2Ph), 2.75–2.85 (dd, $J = 8.4$ Hz, 13.5 Hz, 2H, CH_2Ph), 2.48–2.57 (m, 2H, CH_2), 2.33–2.41 (m, 2H, CH_2), 1.94–1.96 (m, 2H, CH_2), 1.75–1.93 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ167.6, 153.9, 137.5, 130.4, 129.4, 128.5, 127.5, 126.5, 121.2, 71.8, 67.2, 49.4, 42.0, 41.5, 31.2, 28.3. EI MS (*m/z*): 708 (M^+). Anal. Calcd for $C_{38}H_{34}Br_2N_2O_2$: C: 64.24, H: 4.82, N: 3.94. Found: C: 64.29, H: 4.93, N: 3.61.

P2. This polymer was prepared following the similar procedures used to prepare polymer **P1**. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.50–8.10 (m, 12H, Ar–H), 7.15–7.50 (m, 10H, Ph–H), 5.38–5.56 (m, 2H, CH–N), 4.76–4.96 (m, 2H, CH_2–O), 4.24–4.44 (m, 2H, CH_2–O), 2.64–3.16 (m, 4H,CH_2–CH_2), 1.92–2.36 (m, 8H, CH_2-CH_2 and C–CH_2), 0.60–1.30 (m, 22H, C_5H_{11}). ^{13}C NMR-($CDCl_3$, 75 MHz, ppm): δ 169.2, 153.1, 142.4, 140.7, 140.3, 140.0, 138.5, 128.8, 127.7, 126.3, 123.1, 121.4, 120.2, 120.1, 76.5, 75.5, 67.0, 55.3, 49.5, 42.9, 40.5, 32.0, 31.5, 29.8, 29.0, 23.9, 22.6, 14.01, 13.96. Anal. Calcd for $C_{61}H_{62}N_2O_2$: C: 85.67, H: 7.31, N: 3.28. Found: C: 84.81, H: 7.11, N: 3.01.

P3. This polymer was prepared following the similar procedures used to prepare polymer **P1**. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.45–8.10 (m, 12H, Ar–H), 7.15–7.45 (m, 10H, Ph–H), 4.50–4.74 (m, 2H, CH–N), 4.25–4.44 (m, 2H, CH_2–O), 4.07–4.25 (m, 2H, CH_2–O), 3.20–3.40 (m, 2H, CH_2Ph), 2.50–2.98 (m, 6H, CH_2-Ph and CH_2–CH_2), 1.80–2.30 (m, 8H, CH_2), 0.50–1.30 (m, 22H, C_5H_{11}). ^{13}C NMR($CDCl_3$, 75 MHz, ppm): 168.1, 153.3, 151.7, 140.2, 138.5, 137.7, 129.5, 128.6, 126.6, 126.0, 122.9, 121.3, 120.3, 72.0, 67.4, 55.3, 49.4, 42.5, 41.9, 31.5, 29.8, 23.9, 22.6, 14.0. Anal. Calcd for $C_{63}H_{66}N_2O_2$: C: 85.67, H: 7.53, N: 3.17. Found: C: 84.98, H: 7.39, N: 3.01.

Compound 10. To the suspension of NaH in 50 mL of anhydrous THF was added a solution of **9** (0.51 g, 1.0mmol) in 10 mL of anhydrous THF. After the mixture was stirred for 10 min, 2-bromoethylmethyl ether (1.5 g, 1.1 mmol) was added. The mixture was stirred overnight and filtered. After removal of solvents, the residue was washed with petroleum ether to give 0.60 g (88%) of the product as a white solid. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 8.61–8.64 (d, 2H, $J = 7.5$ Hz, Ar–H), 7.43–7.47 (d, 2H, $J = 8.7$ Hz, Ar–H), 7.34–7.39 (t, 2H, $J = 7.5$ Hz, Ar–H), 7.09–7.15 (t, 2H, $J = 7.5$ Hz, Ar–H), 6.66–6.69 (d, 2H, $J = 7.5$ Hz, Ar–H), 6.48–6.52 (d, 2H, $J = 8.7$ Hz, Ar–H), 3.44–3.52 (2H, m, CH_2), 3.54–3.64 (2H, m, CH_2), 3.08 (6H, s, CH_3), 2.86–3.06 (4H, m, CH_2). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 154.0, 147.9, 141.7, 141.5, 133.5, 128.1, 127.0, 123.1, 122.8, 112.9, 107.6, 70.3, 68.1, 59.0, 29.4. EI MS (*m/z*): 620 (M^+). Anal. Calcd for $C_{31}H_{26}Br_2O_4$: C: 59.83, H: 4.21. Found: C: 60.11, H: 4.36.

P4. This polymer was prepared following the similar procedures used to prepare polymer **P1**. ^1H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.90–8.10 (m, 2H, Ar–H), 7.50–7.80 (m, 4H, Ar–H), 7.15–7.40 (m, 4H, Ar–H), 6.90–7.15 (m, 4H, Ar–H), 6.65–6.90 (m, 4H, Ar–H), 3.55–3.87 (m, 4H, CH_2), 2.90–3.20 (m, 10H, CH_2OCH_3), 1.90–2.30 (m, 4H, CH_2), 0.65–1.30 (m, 22H, C_5H_{11}). ^{13}C NMR-($CDCl_3$, 75 MHz, ppm): δ 154.3, 151.0, 148.9, 148.8, 142.2, 141.1, 140.2, 135.8, 131.5, 131.3, 128.6, 128.1, 127.2, 126.5, 124.5, 123.9, 123.0, 122.8, 119.9, 111.9, 70.5, 68.3, 62.9, 59.0, 58.8, 55.6, 40.5, 32.2, 31.8, 31.5, 30.2, 29.9, 29.7, 24.3, 22.6, 14.1. Anal. Calcd for $C_{56}H_{58}O_4$: C: 84.60, H: 7.35. Found: C: 84.39, H: 7.45.

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